explain the relation (3) by the chain mechanism of hydrocarbon combustions, it should be necessary to modify the elementary reactions assumed in the derivation of equation (3)[7] considering that the triple collision process might be included. It may be considered that inapplicability of the relation (4) to C_2F_4–O_2 mixtures is due to the lower total pressures and to the different influence of the pressures upon the mechanism of chain branching, propagating and terminating processes.

Compared with equation (2), the relation (3) may be rather applicable to this explosion.

Part II Explosive Phenomena of Gaseous Acetylene-Oxygen Mixtures

Results

The explosion limits of gaseous C_2H_2–O_2 mixtures were determined at specified compositions, using glass reaction vessels of 1 cm, 2 cm and 3 cm diameters, and are shown in Figs. 2. 1 a (95% C_2H_2), 2. 1 b (90% C_2H_2), 2. 1 c (80% C_2H_2) and 2. 1 d (70% C_2H_2). The experiments on the

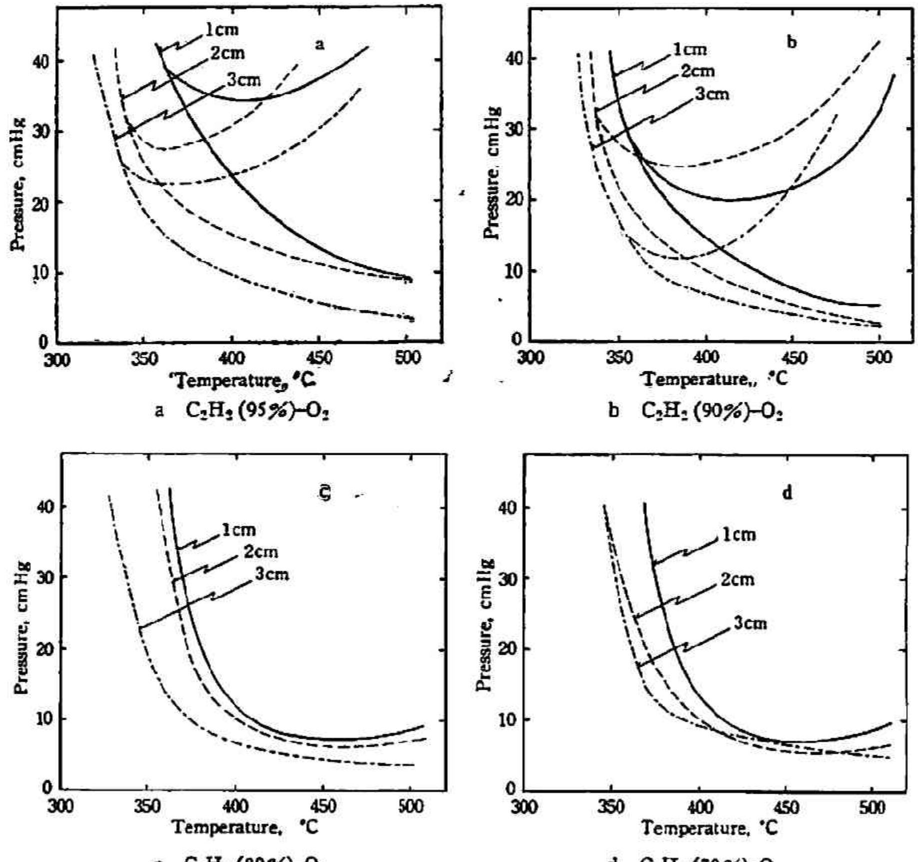

Fig. 2. 1 a, b, c, d Relations between temperature and pressure of explosion limits at specified compositions

7) K. J. Laidler, *Chemical Kinetics*, McGraw-Hill Book Co., p. 319 (1950)

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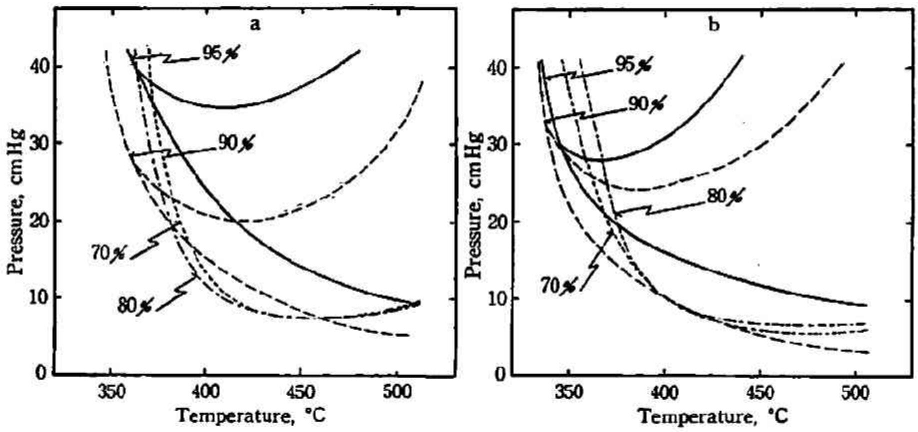
mixtures containing more oxygen have short induction periods of less than 0.5 second, and are dangerous in the apparatus made of glass owing to catching fire to the reservoir.

It is remarkable as described below that the explosion regions of the mixtures containing 95% C_2H_2 and 90% C_2H_2 (Figs. 2. 1 a and b) are separated into two parts where red flames are observed in the higher part and pale-blue flames in the lower part. The minimum of the explosion limit curve shown in the higher (red flame) explosion limits has been reported in the result[2] obtained by the admission method as in the present experiment, but the regions of pale-blue flames have not yet been determined.

The color of the red flames becomes brighter with increasing oxygen content and the temperature of the flames becomes higher.

As to the effect of the diameter of the reaction vessel on the explosion limits, the limits become higher with decreasing diameter as shown in Figs. 2. 1 a, b, c and d. The effect is remar-



a vessel diameter, 1 cm b vessel diameter, 2 cm

Fig. 2. 2 a, b Relations between temperature and pressure of explosion limits in the vessel of a definite diameter

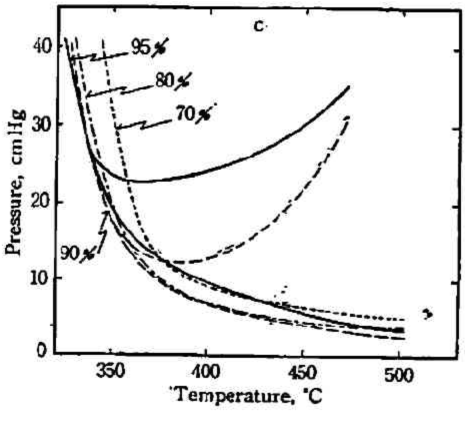


Fig. 2. 2 c Relations between temperature and pressure of explosion limits in the vessel of 3 cm diameter

kable in poor oxygen mixture in the order of 95%, 90%, 80% and 70% C_2H_2 mixtures. In other words, the effect is much remarkable in the condition where the explosion is gentle and less remarkable in the violent explosion.

The plots of the explosion limits at varying compositions in the vessel of the same diameter are shown in Figs. 2. 2 a (1 cm), 2. 2 b (2 cm) and 2. 2 c (3 cm). Considering these diagrams, the change of the limits with compositions is the most remarkable in the vessel of 1 cm diameter and the lower explosion limits are nearly coincident irrespective of the compositions in the vessel of 3 cm diameter.

The plots of the explosion limits (pressure) against compositions at a definite temperature (400°C) are shown in Fig. 2. 3. In the additional experiments on pure acetylene and 98% acetylene

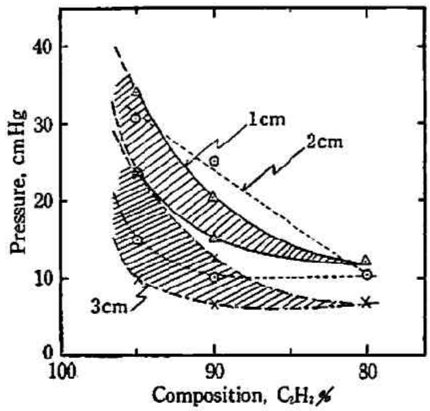


Fig. 2. 3 Relations between pressure and composition of explosion limits at 400°C

mixture, the red and pale-blue flames were not observed even in the severe condition (530°C, 40 cm Hg), so the curves in Fig. 2.3 may rise upwards on the left side. In addition, the regions

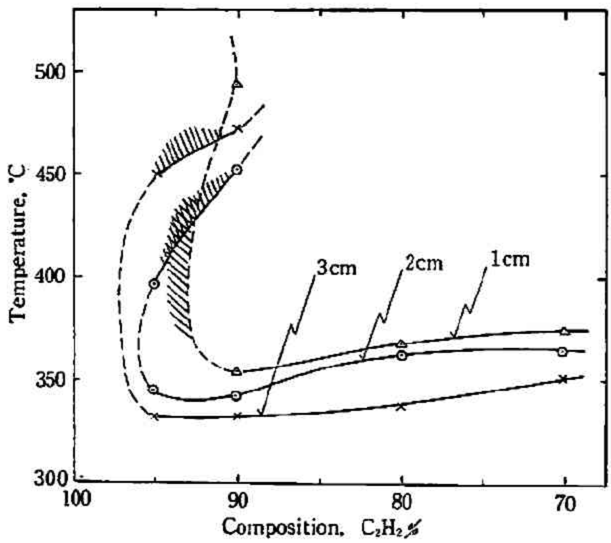


Fig. 2. 4 Relations between temperature and composition of explosion limits at 30 cm Hg

between two curves of each diameter (shaded parts in 1 cm and 3 cm diameters) are the regions of the pale-blue flames.

The plots of the explosion limits (temperature) against compositions at a definite pressure (30 cm Hg) are shown in Fig. 2. 4. The broken curves are also predicted from the additional experiments described above.

Considerations

On the pale-blue flames The pale-blue flames are observed in the gentle explosions of 95% and 90% acetylene mixtures. The lower limits of the pale-blue flames come near to the limits of oxygen rich mixtures as shown in Figs. 2. 2 a, b and c. In the regions of pale-blue flames, the violent explosion does not occur owing to the scanty of oxygen content, and the gentle explosive reaction gives rise to the pale-blue flame.

As the induction period becomes shorter with increasing temperature, the records of pressure-time curves can be obtained only in the range of relatively low temperature owing to the difficulty of experimental manipulation. Fig. 2. 5 shows the pressure-time curves at specified compositions.

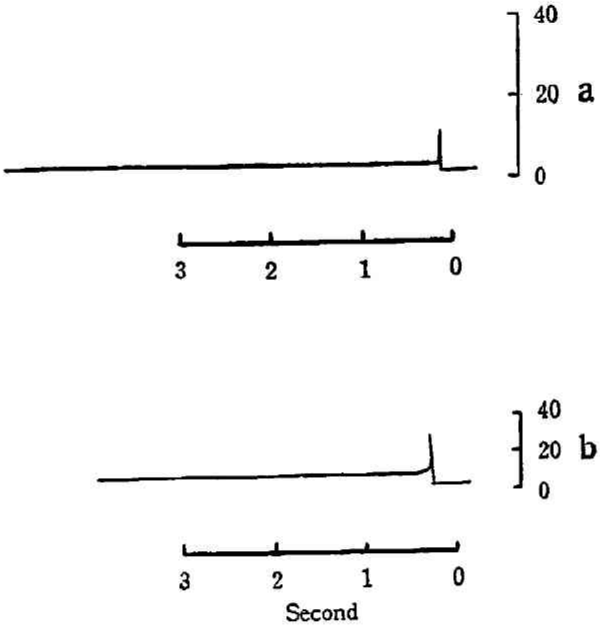


Fig. 2. 5 a, b Typical pressure-time curves at specified compositions of C_2H_2–O_2 mixtures
Ordinate: $\triangle P$ in cm Hg

Curve a Normal explosion with red flame in C_2H_2(70%)–O_2 mixture

Curve b Normal explosion with red flame in C_2H_2(80%)–O_2 mixture

The mixtures of 70% C_2H_2 (Curve a) and 80% C_2H_2 (Curve b) explode violently without pale-blue flames. The mixture of 95% C_2H_2 (Curves c, d and e), however, shows the different forms of pressure-time curves. As described in Part I on C_2F_4 mixtures, the curve of initial pressure increase is concave to the time axis in the region of pale-blue flames (Curve e), but convex to the time axis in the region of red flames (Curve c). And in the intermediate region, the two-stage ignition where the color of the flame changes from blue to red is confirmed by visual observation, but the pressure-time curve (Curve d) does not prove to be the two-stage ignition. The reason

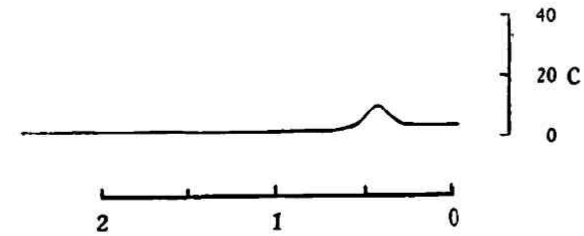
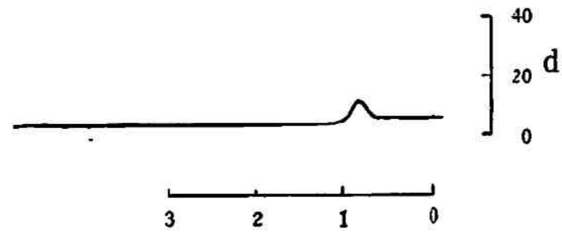
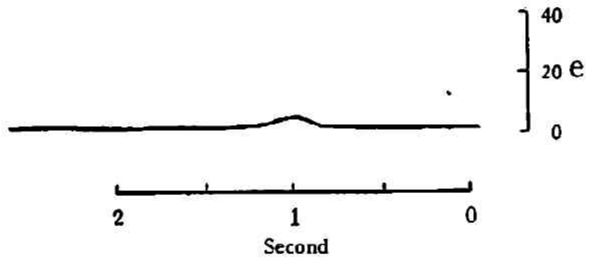


Fig. 2. 5 c, d, e Typical pressure-time curves at specified composition of C_2H_2-O_2 mixtures
Ordinate: ΔP in cm Hg

Curve c Normal explosion with red flame in C_2H_2(95%)-O_2 mixture



Curve d Explosion with two-stage flame in C_2H_2(95%)-O_2 mixture



Curve e Mild explosion with pale-blue flame in C_2H_2(95%)-O_2 mixture

for this may be considered that the heat of reaction is considerably large even in pale-blue flame and does not differ so much from that in red flame, which may be also due to the rapidity of the explosion.

The pale-blue flames are found, accordingly, in the gentle explosions and form the previous stages of the red flames. These natures of the pale-blue flames are the same as those in the case of C_2F_4 and may be considered to be so-called cool flames.* And the pale-blue flames are considered to be found in non-branching chain reaction[5], so the pressure-time curve may become concave to the time axis[4]. In addition, the pressure-time curve in the high temperature range of pale-blue flame region could not be recorded owing to the short induction period. And the experiment was not performed in the high temperature range over 500°C. So we can not predict how to be the region of pale-blue flames in high temperature range.

The explosive reaction may be assumed to be thermal in apparent character in the range shown in Figs. 2. 1 a~2. 1 d where the relations between pressure and temperature in the explosion limits are shown. The plots of $\log P/T$ against $1/T$ are shown in Fig. 2. 6 where the linear

* During the time of printing, we found a report concerning cool flames of C_2H_2-O_2 mixtures (*Combustion and Flame*, **1**, 99 (1957)).

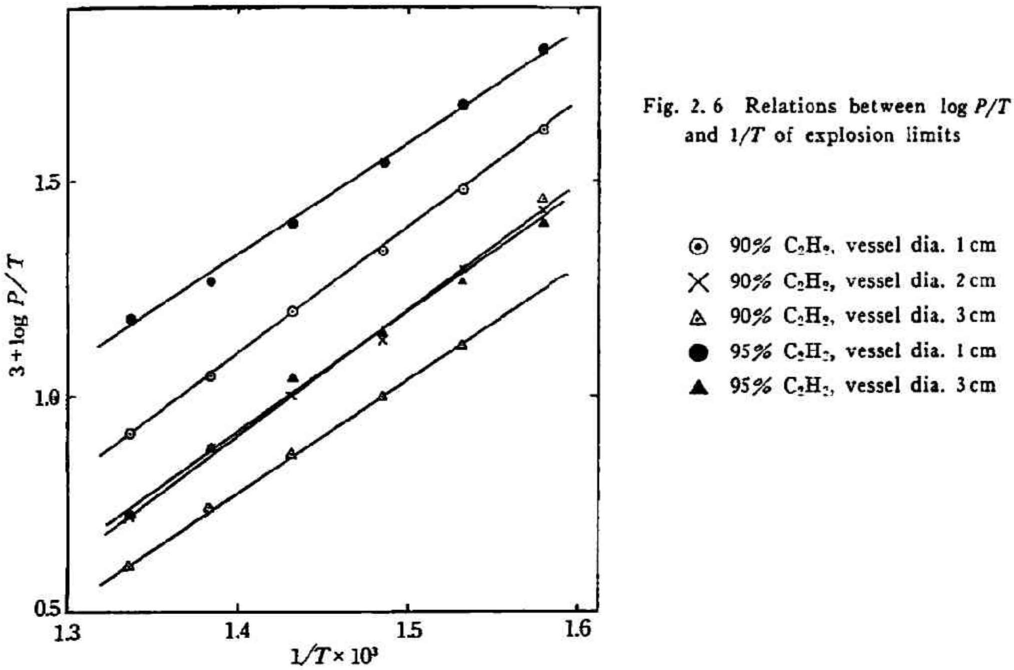


Fig. 2. 6 Relations between log P/T and $1/T$ of explosion limits

relations are obtained in the lower limits of the mixtures of 95% and 90% C_2H_2. The linear relations also hold in the mixtures of 80% and 70% C_2H_2 in the case of 3 cm vessel diameter. From the slopes of these linear relations, the apparent activation energy may be estimated to be about 26 kcal.

The explosion limits of C_2H_2–air mixtures cited from literature[2] were examined by plotting log P/T against $1/T$. The linear relations also hold in the low temperature range. The apparent activation energy calculated, being estimated to be about 28 kcal, agrees with the above value.

From the explosion limits of C_2H_2–air mixtures cited, the relation of

$$P_{C_2H_2}P_{O_2}\left(1+\frac{P_{N_2}}{P_{C_2H_2}+P_{O_2}}\right)=\text{constant}$$

was examined as in the case of C_2F_4 mixtures. The constancy of the relation is not good as compared with the case of C_2F_4 mixtures.

The explosive reactions of C_2H_2 with oxygen or air may be considered to be thermal in apparent character in the present experimental ranges.

The authors wish to express their thanks to Mr. M. Suga and Mr. S. Yoshioka for the assistance done partly in the present investigation and are indebted partly to the Department of Education for the Grant in Aid for Fundamental Scientific Individual Research (The Physico-Chemical Researches on Acetylene) shared out to Prof. Ryo Kiyama.

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